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Non-Stationary Thermoelectric Generators

John G. Stockholm

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Abstract

A review of theoretical publications on non-steady thermoelectrics is given. Review concerns different aspects of non-stationary and pulsed processes in thermoelectric materials and devices. Theoretical analysis of dynamic behaviour of thermoelectric devices, including analysis of small and large signals of thermoelectric generator, is given and details of concepts of quasi-equilibrium thermoelectricity are discussed as well. Special attention is paid to theoretical study of the non-routine regime of non-steady thermoelectricity—fast-time dependence of thermoelectric properties when material or device is well out of equilibrium. Theoretical findings of fast-time dependence give reason to believe that it can increase the output electrical power of thermoelectric generator compared to stationary regime of operation. We also present experimental results obtained with first non-stationary thermoelectric generator prototype, which was designed for operation in fast-time dependence mode. Several research teams are presently making and testing devices to confirm that more electrical power can be obtained in AC mode (AC frequency about hundreds of kHz) than in DC mode. Descriptions with an analysis are given.

Keywords: thermoelectricity, electricity generation, quasi-stationary systems, out-of-equilibrium transient modes, ultra-fast conduction, microscopic processes

1. Introduction

Operation of thermoelectric (TE) heat pumps used for cooling (TECs) and thermoelectric generators (TEGs) are closely related. Results of first theoretical studies of thermoelectric

devices operating in non-steady regimes were published for thermoelectric coolers by Stilbans and Fedorovich in the year 1958 [1]. Then, Gray presented in the year 1960 [2] results of analytical consideration concerning small and large signals of thermoelectric generator. In 1961, Landecker [3] published results concerning fast transient behaviour of Peltier junctions during temperature measurements with thermocouples. Then, in the year 1971 Babin and Iordanishvili studied quasi-stationary thermoelectric generation and in the year 1983, Iordanishvili and Babin published a monograph [4] of non-stationary processes in thermoelectric and thermomagnetic energy conversion systems. It presents the fundamentals of pulsed current generation, pulsed thermoelectric generator, quasi-steady-state generator and single-pulse thermoelectric generator.

There is also non-steady, well-out-of-equilibrium, fast-time dependence. This subject has not been extensively developed and few papers were published on this subject. Such non-steady processes have the potential to transfer higher electrical powers, than in steady state. Currently ongoing experimental work is presented.

2. Theoretical aspects of pulsing

2.1. Two different types of non-stationary phenomena

2.1.1. *Quasi-stationary thermoelectricity*

Quasi-stationary thermoelectricity, that is, quasi-equilibrium thermoelectricity, assumes a slight time dependence and is allowed for all the laws of the equilibrium, which means that this time dependence is only slow in comparison with the microscopic processes of heat transfer and electric conduction. This is considered in detail by Gray [2] and Iordanishvili and Babin [4]. Goupil [5, 6] studied non-stationary operation with Onsager approach and calculates for thermoelectric device the important parameters for transient regimes: time constant τ and capacitance C .

2.1.2. *Far from equilibrium fast-time dependence*

Thermoelectric device developed by Strachan, published by Aspen in the year 1992 [7, 8], was operated in MHz range; unfortunately, functional physics was never established and the unit operated in heat-pump mode and in electricity-generating mode, as well.

The first person who studied the fast-time dependence or well-out-of-equilibrium regime was Apostol [9]. His work can be considered as the beginning of new era in thermoelectric power generation. The physical mechanism is ultra-fast conduction, but this mechanism can be obtained only under certain circumstances, viz.:

- sharp electrical current impulse, associated with shorting of electrical circuit, which produced with appropriate frequency, 'amperage' pulse does not have the time to dissipate, that is, widen, during the time it takes to go around the circuit.

2.2. Quasi-stationary thermoelectricity

2.2.1. Dynamic thermoelectric processes

The study of dynamic behaviour of thermoelectric devices was presented in 1960 by Gray [2]. The object is behaviour of TE energy conversion devices under dynamic conditions. TE generator and TE heat pump also are non-linear distributed-parameter systems. Therefore, it is difficult to exactly analyse their dynamic behaviour. In this study, the dynamic behaviour is investigated by means of linear small-signal-distributed-parameter models, for which useful analytical results are obtained. Analysis allows predicting the dynamic behaviour of thermoelectric device both in frequency-domain and in time-domain equalization algorithms. This can be used to assess quantitative effects of device parameters with regard to dynamic response of the device. It is possible to linearize system's equations in small-signal variations in order to obtain linear mathematical models, more amenable to analysis. This approach is of limited usefulness in computing large-signal dynamic behaviour, such as transient processes, when TE generator is turned on. The study of complete small-signal behaviour of TE generators is developed, the results are expressed in terms of frequency-domain transfer functions and procedures are developed, which allow direct calculation of time-domain transients for the case of input and disturbance time functions, which are Fourier transformable. Experimental observation of small-signal dynamic behaviour of simple heat pump is presented and it confirmed theoretical model. No measurements were made on TE generator, but the accuracy of description should be as good, because mathematical model and analytical techniques are identical.

Comparison of experimentally obtained large-signal static and small-signal dynamic behaviour of TE heat pump with corresponding theoretical results indicates a disagreement at large currents due to neglecting of temperature dependence of parameters.

Complete set of equations for the case of large-signal dynamic analysis for step changes in current is presented.

To conclude, all this work with many equations is the basis for all studies related to small and large signals and it is written in view for appropriate control of TE generators.

2.2.2. Non-stationary processes in thermoelectricity

The subject of non-stationary thermoelectricity is also presented in detail in 1983 by Iordaniashvili and Babin [4]. Several very interesting examples of TE generators are presented, including the case of solid body fuel (SF), capable of producing uniform heat production throughout the volume.

Thus, SF must maintain solid-state properties after heat production process (combustion).

Using the model of semi-infinite rods, assume that at time $t = 0$ there is instantaneous heat production, after which SF temperature becomes equal to T_ω (initial temperature of two bodies is T_0). The system temperature as a function of position and time was calculated and the graph is given (**Figure 1**). Such a generator has high speed and stability of the output characteristics.

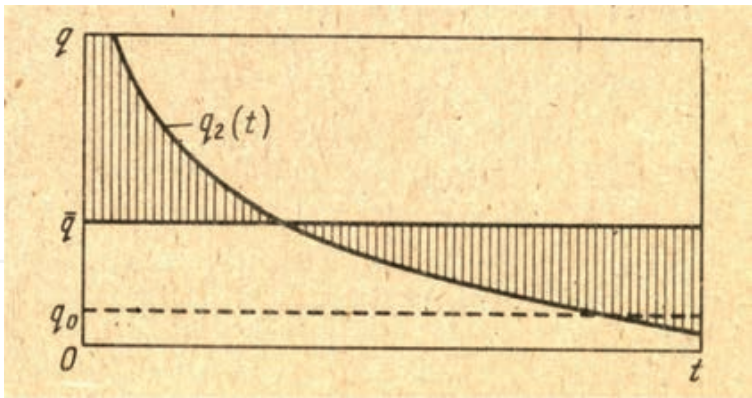


Figure 1. Heat flux q versus time t , \bar{q} is the average effective heat flow during time t , q_0 is the average effective heat flow in stationary mode, $\bar{q}/q_0 \approx 3$.

This graph $q(t)$ shows that in this model, due to thermal conductivity, average, during time t , effective value of heat flow \bar{q} is three times higher than the average effective heat flow q_0 in classic TEG, operating in stationary mode.

Consideration of non-stationary mode includes the following parameters: energy capacity, speed of response, response time improvement, temperature dependence of physical parameters and output characteristics, accounting for Peltier heat production, effectiveness of side-surfaces thermal insulation and thermal stabilization based on the model of finite length. All this information can be very useful for researchers working in the field of transients.

2.3. Thermoelectricity in systems far from equilibrium

M. Apostol in the year 2000 has presented theory of ultrafast thermoelectric conduction [9]. The theory was developed and described [10–12]. It is about moving heat pulse along a rod of thermoelectric material of length 1 mm with on and off connection along a wire 1 cm long. The electrical power is extracted along this wire. A sketch of the pulses is below (**Figure 2**).

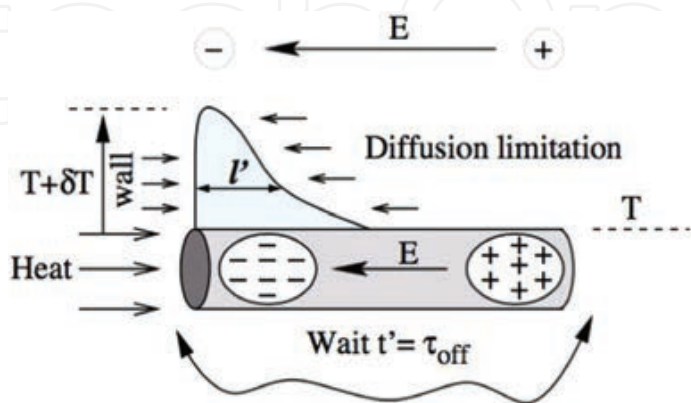


Figure 2. The pulse is deflated of heat at the cold end and another pulse is constructed at the hot end. T is the temperature, δT is the variation in temperature, t' is time off, which is the time between 2 pulses.

The shape of the wave as a function of time t and distance x is $n(x,t)$ [10]:

$$n(x,t) = \frac{V \times \delta_n}{\sqrt{2\pi \times \Lambda \times \nu \times \tau}} \times \exp\left(-\frac{x^2}{2\Lambda \nu t}\right), \quad (1)$$

here V original volume of δ peak; δ_n is quasi-particle density in δ peak, Λ is mean free path of quasi-particles; t is time; ν is transport velocity.

The width of the pulse is expressed as:

$$l = \sqrt{\Lambda \times \nu \times \tau_{\text{off}}}, \quad (2)$$

where l = width of pulse, τ_{off} = time off.

He gives the relation of maximum power output $P_{\text{ext}}^{\text{max}}$ with pulses of ultrafast conduction compared to maximum power in DC mode $P_{\text{dc}}^{\text{max}}$ as:

$$P_{\text{ext}}^{\text{max}} = 2 \frac{l}{\sqrt{\Lambda l}} \times P_{\text{dc}}^{\text{max}}, \quad (3)$$

$$P_{\text{ext}}^{\text{max}} = 60 \times P_{\text{dc}}^{\text{max}}. \quad (4)$$

The ratio of 60 is theoretical value calculated with some assumptions. Even when the experimental ratio is much smaller than 60, then the output power $P_{\text{ext}}^{\text{max}}$ can be many times greater than the DC mode value. This can be the major breakthrough that we are searching for to 'beat' material limitation of $ZT = 2$.

3. Pulsed mode thermoelectric generators

3.1. Thermoelectric generator working on MHz frequency

3.1.1. Primary patents and papers

Priority on thermoelectric energy conversion in high-frequency mode was filed by Aspen and Strachan in the years 1990–1991 [13]. In the year 1992, Aspen and Strachan published results of development and demonstration tests of MHz thermoelectric generator [7, 8]. This is the first example of thermoelectric device operating far from equilibrium.

3.1.2. Description of thermoelectric device operating far from equilibrium

Strachan develops a vibrator to break kidney stones. He discovered that his device could operate as a heat pump (to produce ice) or, with temperature difference between two sides, it could generate electrical power sufficient to operate a small fan. Experimental study was done in collaboration with Oxborrow. It was headed by John Stockholm of Marvel Thermoelectrics and was financed by automobile company PSA.

John Stockholm and M. Almeida from Supélec visited Scott Strachan in his office at the Technology Transfer Centre, University of Edinburgh, Scotland, in February 1996. The device built by Scott Strachan over a year ago was no longer operational, as it had degraded with time, but he showed a video and gave us a copy of it.

He was extremely open and gave a great deal of advice on how to make a unit.

A 'still' from the video is shown in **Figure 3**.

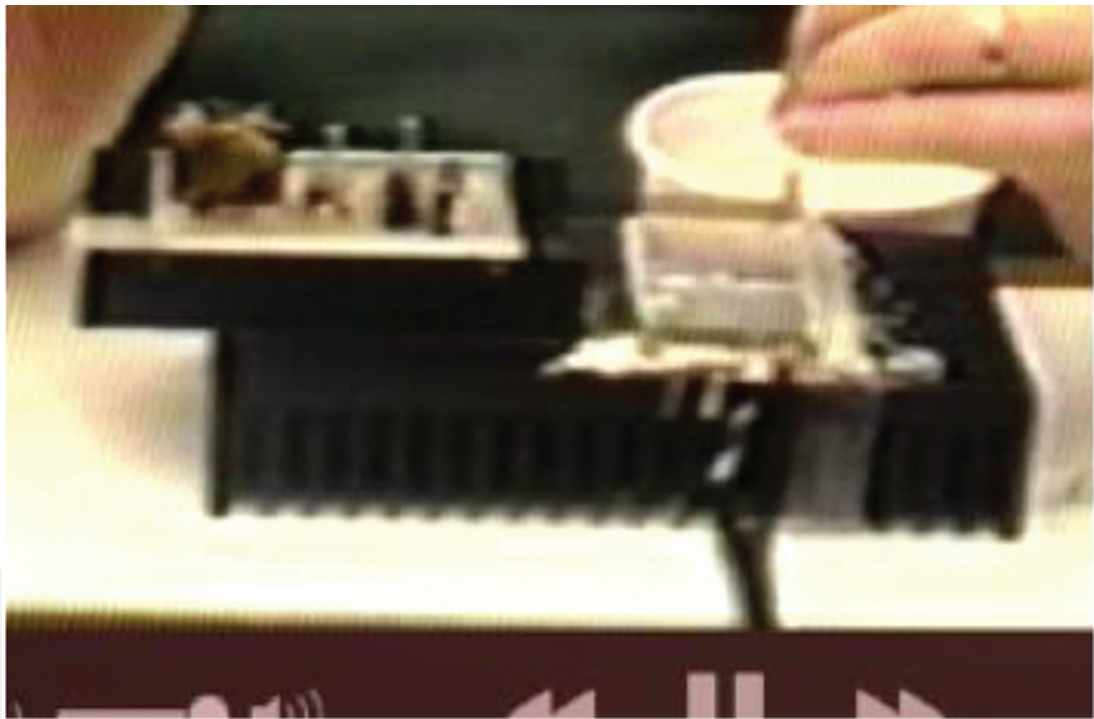


Figure 3. Scott Strachan operating the device.

Thermoelectric generator is located below his fingers, below the square white box, into which Scott Strachan pours hot water to generate ΔT across both sides of TE generator.

It is a small multi-layered device 30×2.5 mm (ΔT is across dimension 2.5 mm) consisting of stack: Al film—Ni film—piezoelectric film (PVDF)—ethyl cyanoacrylate adhesive—Fe film on BASF recording tape—Mylar, BASF recording tape—ethyl cyanoacrylate adhesive—Al film; repeat periodically (**Figure 4**). A device of several cubic centimetres in volume is vibrated by PZT at 500 kHz. It produces 0.14 W of electrical power from heat throughput of 3.7 W.

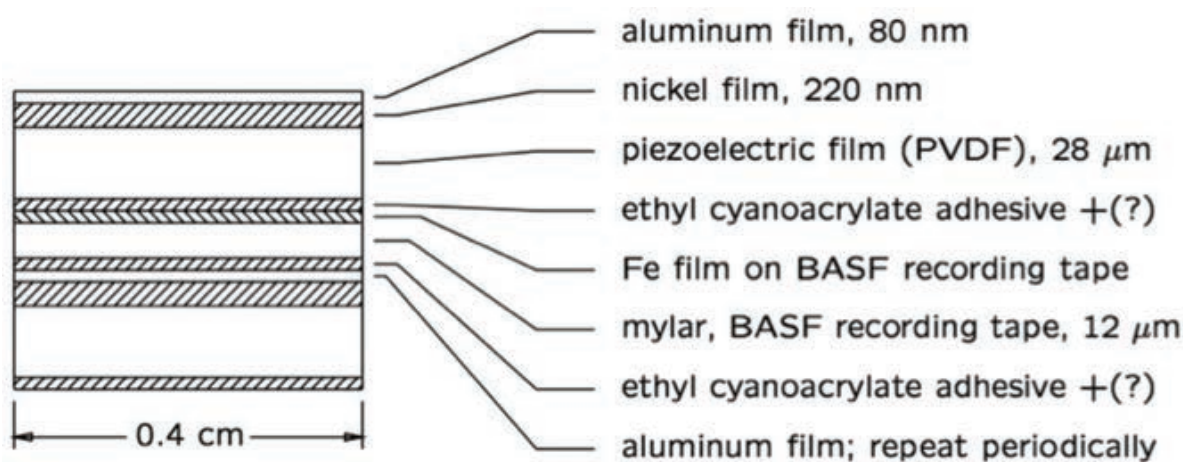


Figure 4. Strachan device-stack of different materials.

Energy conversion efficiency calculated from the above values is equal to 4%. This is very high, considering that ΔT is below 75 K (boiling water and ambient air), compared to bismuth telluride, which for similar ΔT would give much less than 2%.

Two prototypes were made by Mark Oxborrow.

Prototypes are very difficult to make, in particular with ‘super glue’, if the sheet is badly placed, one has to start the assembly process all over again.

The one, he sent to Supélec, was destroyed during testing and John Stockholm terminated the study, as it was apparent that the device was not adaptable to powers required for automobiles.

Our objective was to test the device, then to make similar more simple devices to determine the key components, but we were not successful in even reproducing the device.

Many people showed an interest in Strachan’s device. Details of TE generator were given, in presentation by Maynard and Mahan of Penn State at ICT2005 in Clemson SC [14]. Also, people from MIT showed interest in Strachan’s device. But nobody was able to make the device following all advices from Scott Strachan. All those involved have doubts about the theoretical aspects described by Harold Aspen, who by profession was a patent attorney.

It is incredible that Strachan’s work could not be reproduced and devices made to determine the key technical parameters. He was pioneer in the realization of far-from-equilibrium regime of TE device by pulsing in MHz range.

3.2. Schroeder’s pulsed TE generator

In the year 1994, Jon Schroeder announced a ring-shaped TE generator pulsed at 60 Hz and he published a paper about it in the year 1999 [15].

A prototype was shown to visitors, but only measurement on one thermoelectric couple was made. This measurement was used to calculate the output electrical power of the ring, but thermoelectric generator did not work.

Only in 2004, TE generator prototype with bismuth telluride elements, pulsed at 200 kHz, was demonstrated. But only the output electrical power of prototype was measured. So, we did not know if pulsed-operated TE generator produced greater efficiency than standard DC-operated TE generator with bismuth telluride couples operated within temperature limits of bismuth telluride.

In 2008, Marin Nedelcu with a friend visited Jon Schroeder in Leander, Texas. A video was made showing Jon Schroeder operating the device.

The electrical conversion efficiency was calculated as exceeding two times the DC mode efficiency. A photograph taken from the video made by Marin Nedelcu is shown in **Figure 5**.



Figure 5. Schroeder’s pulsed TE generator.

The unit weighs about 12 kg. Heat source is from propane in a bottle and cold source is from Blades facing downwards immersed in water.

Schroeder ring. It consists of a ring designed by Jon Schroeder, described in a patent [16]. The heat is produced in the centre by hot gases; gases can be combustion gases from natural gas. The heat is transferred by convection and radiation to the radial blades ‘hot’ (**Figure 6**).

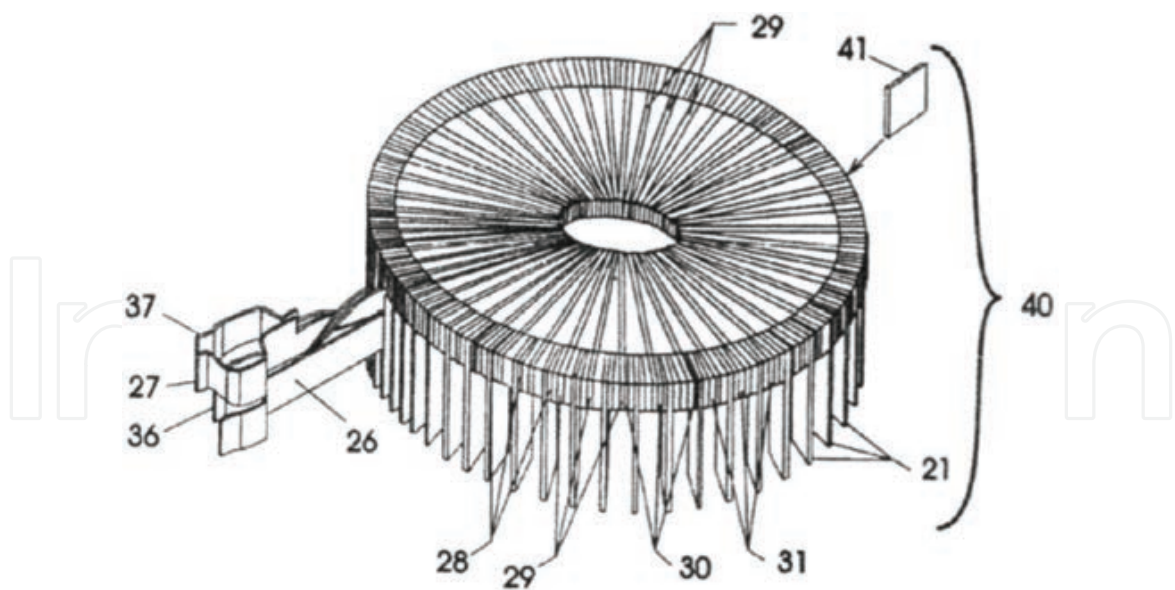


Figure 6. Schematic of Schroeder's ring. The ring is 250 mm diameter. The cold blades 21 are oriented downwards and are cooled by forced convection. Voltage outlets 36, 37.

Figure 7 shows cross section, with a central burner; hot blades marked 4 are connected to the hot side of the pieces of TE and cold blades are marked 3. The propane is burned in volume 14 and the hot combustion gases exit through the central hole 20.

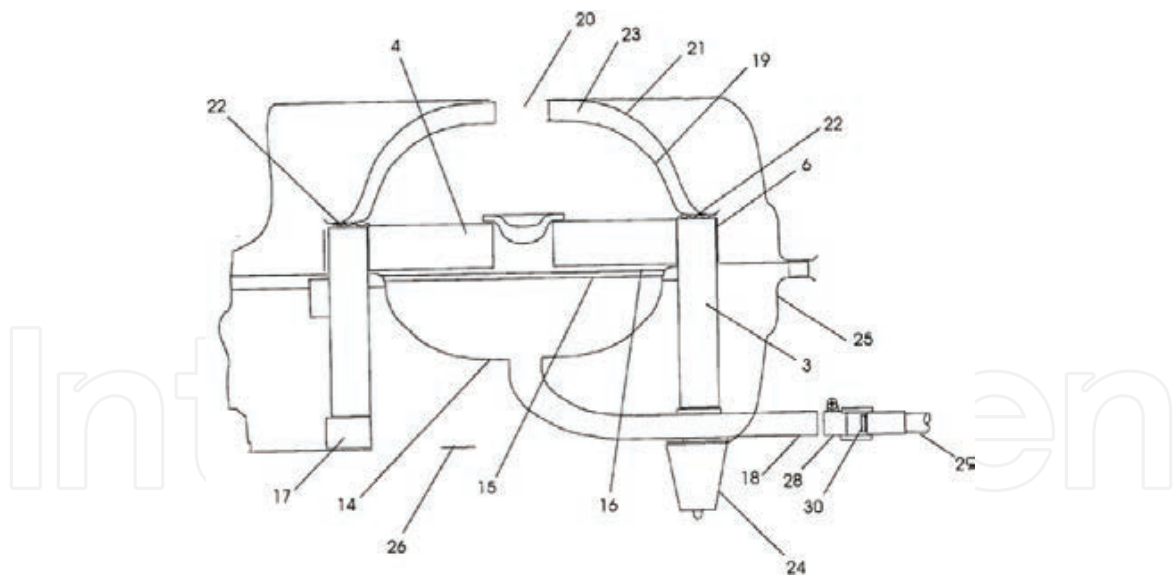


Figure 7. Cross section of the unit.

This schematic shows that radial blades 4 are heated by hot gas; blades 3 facing downwards are air-cooled. Thermoelectric material: bismuth telluride ($20 \times 20 \times 1$ mm), alternatively n- and p-type, is placed between heated and cooled blades. With temperature difference between hot and cold blades, voltage is created at outlets 36 and 37 (**Figure 6**) that are connected to the primary winding of a transformer through MOSFETs, which operate in 100-kHz range.

Output connections of TE generator are connected to two circuits in parallel (not shown).

The secondary winding of a transformer increases the voltage. The switching between two circuits (primaries wound in different directions of a transformer) is done before opening the circuit, so one primary winding is always connected to TE generator. In this way, electrical current is pulsed at around 200 kHz, then rectified and can be converted into AC current, for example, 220 V.

4. Impedance of thermoelectric devices

We examine values obtained from three different approaches of the impedance:

- First approach is theoretical. Finite time thermodynamic (FTT) approach is used by Goupil [5]. The development of Novikov-Curzon-Ahlborn description of TEG has demonstrated that there exists a close feedback effect between the output electrical load value and entering heat flow.
- Second approach is experimental. Low-frequency impedance spectroscopy technique of thermoelectric modules was proposed by García-Cañadas [17].
- Third approach is theoretical; it is proposed by Apostol [9].

4.1. Onsager equations

Onsager equations are for stationary systems; equations can be extended to non-stationary conditions as presented by Goupil [5].

Assuming that the entropy per charge carrier expression is:

$$A = -e \times \alpha, \tag{5}$$

α is Seebeck coefficient, e is charge of the electron.

The others terms derive directly from the thermo-elastic coefficients of the electronic gas,

$\tau_0 = \frac{e^2 \chi_T}{G}$, $l = \frac{C_N}{T \chi_T}$, $L = \frac{e^2 K}{GT}$, where K and G are, respectively, thermal and electrical conductance of the system. We also have the specific heat:

$$C_N = \frac{T}{N} \times \left(\frac{\partial S}{\partial T} \right)_N, \tag{6}$$

χ_T is the isothermal compressibility, S is the entropy:

$$\chi_T = \frac{1}{N} \times \left(\frac{\partial N}{\partial \mu} \right)_S, \quad (7)$$

with N the number of carriers and μ the electrochemical potential. After calculation of the eigenvalues and eigenvectors, we get the complete expressions of the transient response of the system. In most of the cases, the thermal and electrical time constants, respectively, τ_{thermal} and τ_{elec} , are mixed together in a complicated way, but two extreme cases can be considered:

– Under very weak coupling, $A \ll L/l$, we find classical results, $\tau_{\text{elec}} = \tau_0$ and:

$$\tau_{\text{thermal}} = \tau_0 \frac{l}{L}; \quad (8)$$

– Under strong coupling condition, $A \gg L/l$, thermal time constant diverges and electrical time constant becomes:

$$\tau_{\text{elec}} = \frac{C_N}{\chi_T e^2 \alpha^2 T} \tau_0 = \frac{C_N}{\alpha^2 G T}. \quad (9)$$

Since G is the resistive part of the impedance, the reactive part gives the expression of the so-called ‘thermoelectric capacitance’:

$$C_{TE} = \frac{C_N}{\alpha^2 T}. \quad (10)$$

Thermoelectric time constant of the system is then finally:

$$\tau_{TE} = R_{TE} C_{TE}. \quad (11)$$

Reference [5] gives all the intermediate steps and the result is thermoelectric capacitance:

$$C_{TE} = \frac{3Nk}{\alpha^2 T}. \quad (12)$$

Assuming standard sample with parameters close to room temperature, ($V' = 1 \text{ cm}^3$, $n = 5 \times 10^{19} \text{ cm}^{-3}$, $T = 400 \text{ K}$, $\alpha = 160 \text{ } \mu\text{V K}^{-1}$), we get:

$$C_{TE} = \frac{3Nk}{\alpha^2 T} \approx 202 \text{ F}. \quad (13)$$

Complete internal resistance of the system is now replaced by internal impedance:

$$Z_{in} = R_{TE} // C_{TE} + R. \quad (14)$$

This result shows that the internal resistance is larger at zero frequency (stationary conditions), // means that R_{TE} and C_{TE} are electrically in parallel, $(f=0) = R_{TE} + R$, than it is for high frequencies, $Z_{in}(f=0) = R_{TE} + R$, then it is for high frequencies, since R_{TE} term becomes short-circuited by C_{TE} giving $Z_{in}(f > 0) = R$.

$R_{TE} \approx R \approx 10^{-4}$ Ohm; $\tau_{TE} \approx R_{TE} C_{TE} \approx 2 \times 10^{-1}$ s, which gives low-pass filtering at really low frequencies. Depending on precise values of internal isothermal resistance, low-pass filtering effect may be found in the range from 1 kHz to 1 MHz.

4.2. Spectroscopic impedance

Spectroscopy analysis of thermoelectric devices has been performed by García-Cañadas [17] and Gao Min [18]. They have studied thermodynamics of thermoelectric phenomena by frequency-resolved methods, which show that TE devices have a capacitive component that can be exploited to improve performance.

4.3. Basics of pulsed-operating thermoelements

Apostol and Cune [11] show how electrical circuit of thermoelectric device can be represented with electrical resistance in series and capacitor in parallel.

5. Experimental devices

5.1. Extraction of electrical power

Electrical power from DC-operated TE systems is most commonly extracted on electrical load resistance. Recently, pulse-width modulation (PWM) with matched load has been used, especially, when powers and voltages are small. In the case of pulsed systems, we have already AC system, so PWM is the logical way to extract electrical power.

When we have DC-operated thermoelectric generator, then power is extracted on resistive load. The maximum power is extracted, when external load resistance R_L is equal to the resistance of power source R_S . It was shown in 2001 by M. Nedelcu and J. Stockholm that when electrical current was pulsed at 50 kHz, then the electrical output power was constant at $R_L < R_S$. This observation showed that small electrical resistance, such as impedance, might be of interest to extract electrical power efficiently.

Equivalent electrical circuit contains electrical resistance of thermoelectric material, capacitance in parallel, to which one can add an inductance composed of the primary winding of a transformer to extract electrical power at voltages of usable values. Today, there are no mathematical models to dimension such circuits.

Spectroscopic impedance measurements made on commercial thermoelectric modules (e.g., 40×40 mm with 127 couples) have shown very high values of capacitance in Farad range. We are dealing with super-capacitors, which can be operated at more than 100 kHz. Several teams are designing and making different units to check ultra-fast conduction theory.

5.2. Devices

Jon Schroeder built the first high-frequency-operated generator, but, unfortunately, he has not been able to make a second unit. There are explanations. The ring design is the ideal design, but it has major flaws: when a generator is operated and stopped, the ring expands and contracts creating shear stresses on a thermoelectric material; these stresses degrade bismuth telluride material and interfaces with copper. The second flaw is that all thermoelectric discs must be soldered in one operation; chances of success are very small. So, prototypes being built now have column structure, where TE elements are in line and compressed between heat sources, which are placed laterally or in line, when liquid is used.

5.2.1. Column structure

Several teams are working on devices based on the column structure.

5.2.1.1. Column design by Nedelcu

A team headed by Marin Nedelcu in Bucharest started by building ring units with individual water cooling for each bismuth telluride disc, but following problems of water leaks abandoned the ring and resorted to column structure. M. Nedelcu used in column design bismuth telluride discs: $D = 24$ mm and 1 mm thick; he built several columns, the latest is shown in **Figure 8**.



Figure 8. Thermoelectric column built by Nedelcu.

Nedelcu has built eight columns the same as this one. Each column has seven TE couples plus one at the end, so that both ends are cold. Approximate dimensions of cold blocks are $30 \times 35 \times 8$ mm with two holes with a diameter of 4 mm. Hot plate is attached to the top flat surfaces; water flows through the holes through the cold side, which are connected by rub-

ber u-bends, not shown. The water is distilled and has high electrical resistance. The assembly is on-going and testing is planned.

5.2.1.1.1. *Commercial module design*

Recently, Nedelcu built TE generator using four commercial electricity generating modules connected electrically in parallel, with total electrical resistance around 30 mOhm. Modules are assembled between water-cooled plate at $T \sim 38^{\circ}\text{C}$ and heated plate at $T \sim 188^{\circ}\text{C}$, heating power with 170 V and 5.9 A = 1003 W.

Electrical current output was pulsed using MOSFETs at around 200 kHz. The output current from the transformer is rectified. The load is 100 W filament electrical light bulb. Measured voltage is 210 V and current is 0.4 A, so electrical power output is 84 W. So, overall efficiency (including heat losses) is 8.4%; this is about two times higher conversion efficiency, when operated in DC mode.

These measurements seem to confirm that pulsing can improve efficiency due to ultra-fast conduction as predicted by Apostol. When dealing with such breakthrough results, one must be extremely cautious and obtain results from another laboratory.

This TE device made by Nedelcu is very different from Schroeder ring (120 slices of bismuth telluride with an area of 4 cm^2 , thickness of 1 mm, all in series electrically); here we have about 71 couples of bismuth telluride (unknown dimensions, can be estimated: area 10 mm^2).

5.2.1.2. *Pulsed TE generators by Krzysztof Wojciechowski team*

A team headed by Krzysztof Wojciechowski of AGH Cracow and Institute of Electron Technology, Cracow, designed and built several small prototypes to detect high-conversion efficiencies by pulsing thermoelectric circuit. First prototype had water-cooled plate at the top and the bottom, see **Figure 9**.

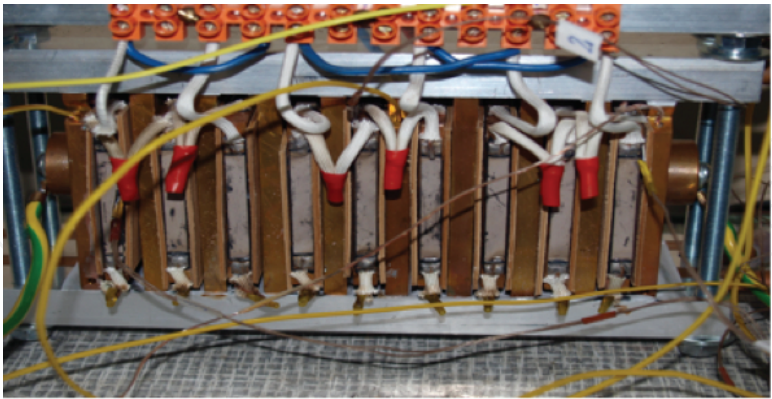


Figure 9. Unit with 18 bismuth telluride discs (n- and p-type).

Figure 10 shows a smaller unit with six TE discs with a diameter of 24 mm and a thickness of 1 mm, aluminium water-cooled plates above and below, electrical heaters at the front and back. Detail of column electrical heater ‘red’ at top and bottom without the water cooled plate, that would be located on the right side and on the left side (**Figure 11**).

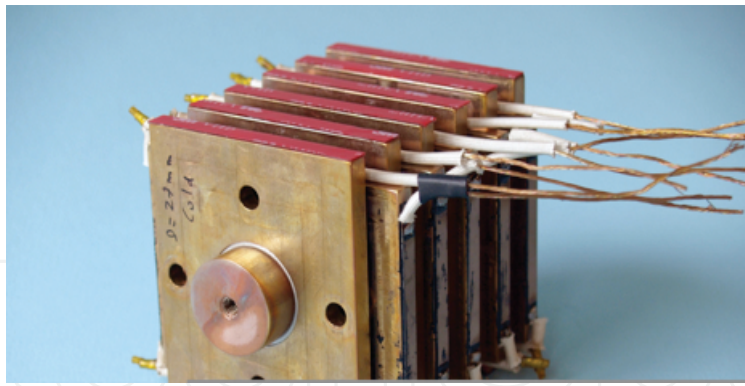


Figure 10. Unit with six bismuth telluride discs—electrical heaters front and back, compact water coolers, see **Figure 12**.

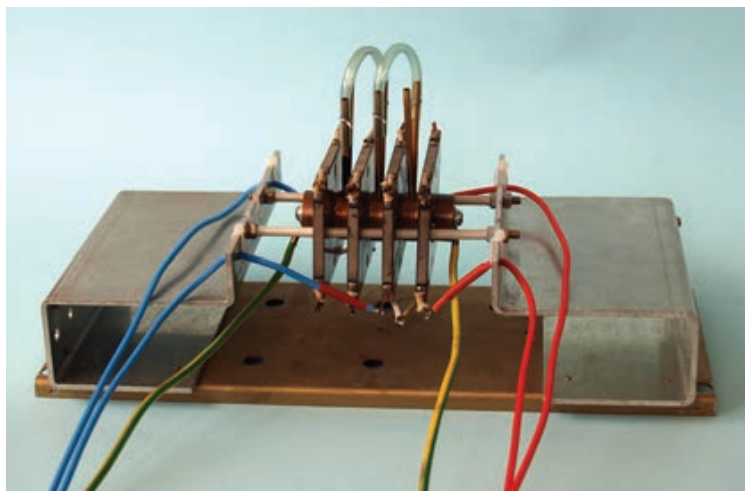


Figure 11. Unit with three TE discs of an outside diameter 24 mm and thickness 2 mm. The heaters are electrical strips on the left and right sides. The cooling is with compact cooler as shown in **Figure 12**.

Thermal and electrical measurements showed that produced voltage was insufficient to operate MOSFET switching. Once again, this confirms the difficulty to have sufficient heat flux through bismuth telluride material, as bismuth telluride has thermal conductivity of about 1.5 W/(m K), so in bismuth telluride disc with a cross section of 4.5 cm² and a thickness of 1 mm, heat flux power at $\Delta T = 100$ K is equal to 67.5 W (**Figure 12**).

5.2.1.3. Unit with column structure by Glick et al

A team with John Stockholm, James Glick and Brad Vier are also building a TE generator unit, which has a column structure. First prototype P1 was built with five couples of bismuth telluride discs with a diameter of 24 mm and a thickness of 1 mm. It was operated with propane combustion gases and cooled by ambient air. The objective was to measure temperatures at the interface of bismuth telluride.

A schematic of pulsed-width modulation electrical circuit is shown in **Figure 13**.

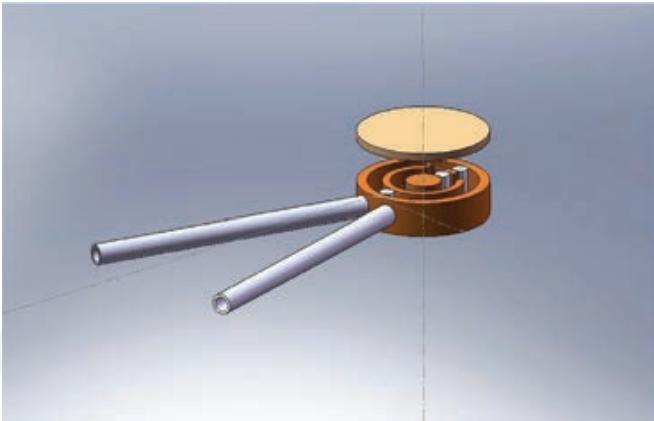


Figure 12. Detail of compact water cooler with an outside diameter of 25 mm placed on the axis of the column.

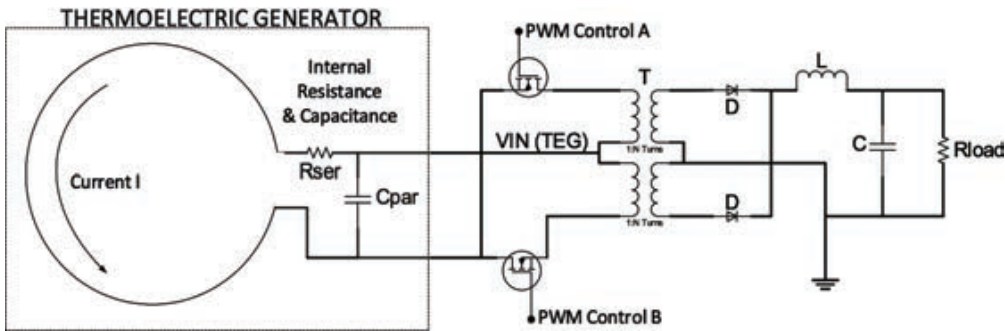


Figure 13. Schematic of PWM controller electrical circuit.

A photograph in **Figure 14** shows a lateral view of the inside of TE generator.

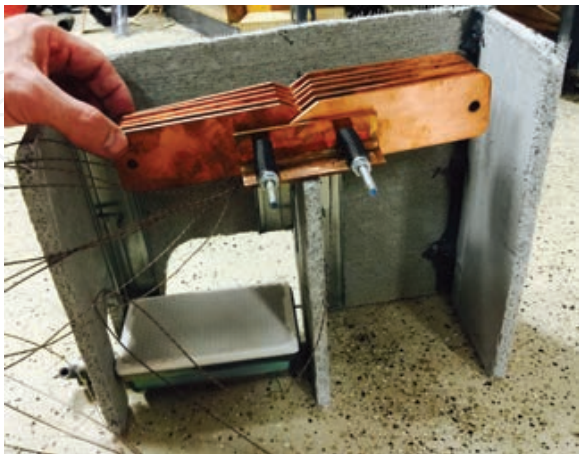


Figure 14. Lateral view of inside of P1 prototype TE generator, left side at the bottom is the infrared burner, combustion gases go upwards; in the centre at top, column structure-heated blades; to the left, cooled blades by ambient air blown upwards (fan is not shown).

Figure 15 shows the top view of TE generator: on the left are heated blades and on the right are blades cooled by air, the white material is to insulate thermally thermoelectric column from hot combustion air. Bismuth telluride disc with copper caps is shown in **Figure 16**.



Figure 15. Top view of inside of P1 prototype.

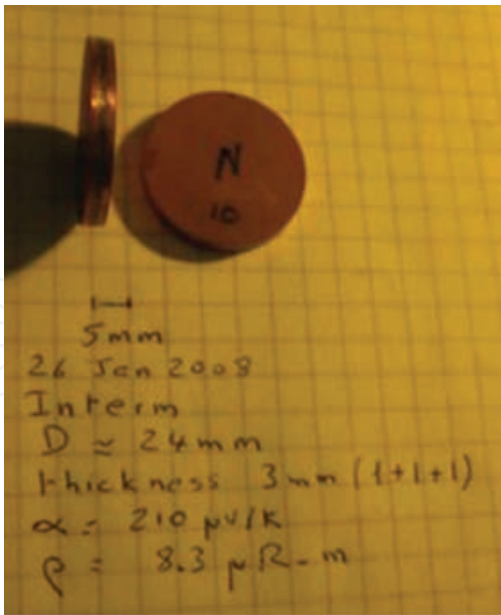


Figure 16. Bismuth telluride disc with copper caps.

When the unit was operated, the propane combustion gases heated and forced ambient air cooled. However, measured temperature difference at the interface with bismuth telluride was

insufficient to operate TE generation, but valuable information was obtained to improve the design.

Stockholm presented in 2014 results concerning different aspects of pulsed TE generator operation, such as high-efficiency pulse-width modulator thermoelectric generator with an active load [19] and transient thermoelectric generator: an active load story [20].

Development is on-going. A prototype designed for measurements is being made.

Figure 17 shows the 10 kW transformer to be installed. **Figure 18** shows four Hi-Z-14 modules. Results will be published as soon as they have been repeated to ensure validity.



Figure 17. PWM 10 kW transformer dimensions $250 \times 190 \times 140$ mm high.

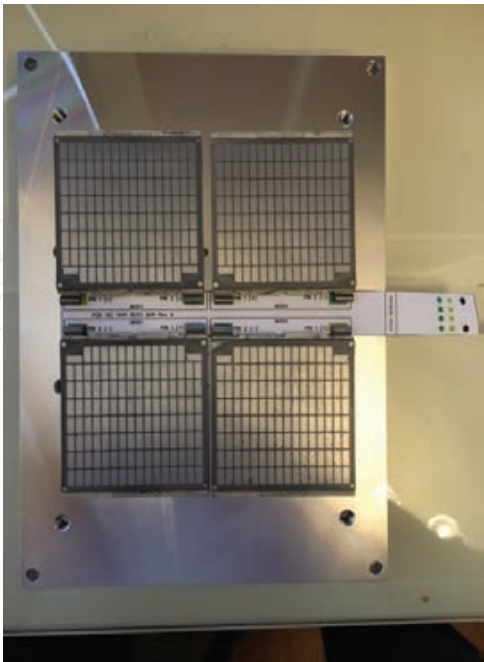


Figure 18. Four Hi-Z-14 modules on a water-cooled plate.

6. Potential of non-stationary far-from-equilibrium TE generators

Very few people have studied the microscopic phenomena of non-stationary, far-from-equilibrium thermoelectrics. Marian Apostol is the main contributor to the subject with many papers. He has shown great potential of this phenomenon. Why is it that 15 years after his first paper nobody has an industrial unit? There are many reasons. People don't believe new phenomena!

Technology of these systems is difficult, because of constraints: high heat fluxes and very low electrical resistances. Electrical currents can be enormous, more than 1000 A and voltages can reach kV. All this is confirmed by the numerous problems encountered by all experimentalists. Strachan had great voltage problems. High-frequency pulsing is not stable. Marian Apostol compares these systems to a sphere on top of a mountain! Prototypes are being built and tested to confirm these high-energy conversion efficiencies.

In 2014, measurements on the unit built by Schroeder were made in his workshop, on a unit not designed for any measurements inside the unit. The only possible measurements were the amount of propane burnt and electrical power output. Measured values of conversion efficiencies exceeded by a factor of more than 2, the values, of equivalent DC-operated unit with similar temperature differences.

Recently, Nedelcu has built a TE device with four commercial electricity-generating modules Hi-Z14 (56 × 56 mm) with 31 bismuth telluride couples. They are electrically in parallel so that the electrical resistance of the load is minimum about 40 mOhm placed between heated plate at 188°C and cold plate at 38°C. He claims that the conversion efficiency exceeds two times the DC conversion efficiency from thermal to electrical power. All these claims need to be repeated in a laboratory and fully documented in particular measurements of electrical pulses and power on primary circuit must be made.

There are also potential sources of degradation at interfaces. Anatol Casian at the University of Moldova is concerned about possible charge carriers' depletion.

Today, several research groups, on very small budgets, are working on devices to confirm experimentally that very high-performing generators are a reality; as soon as there is confirmation, research money will be available. Many theoretical researches are necessary before any transfer to industry.

7. Conclusions and outlook

The operation in non-stationary modes near equilibrium has been presented. Two books, one by Gray (1960) [2] and one by Iordanishvili [4], cover extensively the subject. Recently, Nedelcu et al. [21], Min [18] and García-Cañadas [17] have done experimental spectroscopic analysis of thermoelectric systems, which confirm that TE device is equivalent electrically with a capaci-

tance in parallel with TE generator, which has internal electrical resistance. This is confirmed by theoretical papers by Apostol [9–11] and Goupil [5].

One important advantage of operating in a non-stationary mode is to obtain thermoelectric generators with better performances, than with DC operation. The present-day DC-operated TE generators are limited by ZT of TE material, which is less than 2.

Measurements need to be confirmed by other laboratories. The main interest is energy conversion efficiency. Prototypes have mainly used bismuth telluride, because it is the most suitable for generators operating with the cold side around ambient, but any thermoelectric material could be used.

Prototypes are being built and tested to confirm these high-energy conversion efficiencies, which are predicted by ultra-fast conduction theory of M. Apostol [9].

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Author details

John G. Stockholm

Address all correspondence to: johngstockholm@gmail.com

Marvel Thermoelectrics, Joachim du Bellay, Vernouillet, France

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